

A consistent description of the iron dimer spectrum with a correlated single-determinant wave function

Michele Casula^a, Mariapia Marchi^{b,c}, Sam Azadi^b, Sandro Sorella^{b,c}

^aCentre de Physique Théorique, Ecole Polytechnique, CNRS, 91128 Palaiseau, France

^bSISSA, International School for Advanced Studies, 34014, Trieste, Italy

^cDEMOCRITOS National Simulation Center, 34014, Trieste, Italy

Abstract

We study the iron dimer by using an accurate ansatz for quantum chemical calculations based on a simple variational wave function, defined by a single geminal expanded in molecular orbitals and combined with a real space correlation factor. By means of this approach we predict that, contrary to previous expectations, the neutral ground state is ${}^7\Delta$ while the ground state of the anion is ${}^8\Sigma_g^-$, hence explaining in a simple way a long standing controversy in the interpretation of the experiments. Moreover, we characterize consistently the states seen in the photoemission spectroscopy by Leopold *et al.*[1] It is shown that the non-dynamical correlations included in the geminal expansion are relevant to correctly reproduce the energy ordering of the low-lying spin states.

1. Introduction

The iron dimer is a puzzling molecule. Indeed, explaining all the related experimental findings in a consistent theoretical frame is very hard. Moreover, this dimer represents a testcase to check the ability of a method to capture the physics of the transition metal compounds, since it includes all their difficulties, namely a strong electron correlation in the nearly half-filled d orbitals, and a non trivial ordering of the low-lying energy states which differ by their spin.

In 1986 Leopold *et al.* carried out an experiment[1] of negative ion photoelectron spectroscopy (PES), with the aim of studying the low-lying electronic states of Fe_2 . A sample of Fe_2^- is prepared and excited by an incoming photon. The spectrum of Fe_2 appears remarkably simple, with only two peaks, corresponding to the excitations from the Fe_2^- ground state to those Fe_2 states allowed by the selection rules, which implies that the total angular momentum of the final state cannot change by more than one. Both states reveal the same vibrational frequency and bond length. Few years later, Leopold[2] argued that the simplest explanation of these data is to admit that the ${}^9\Sigma_g^-$ is the ground state of Fe_2 , and the ${}^8\Sigma_u^-$ is the ground state of Fe_2^- . This interpretation is based on the hypothesis that the two-band system observed in the Fe_2^- spectrum is due to the detachment from a $4s$ -like molecular orbital (MO). Therefore, if one supposes that the ground state of Fe_2^- is ${}^8\Sigma_u^-$, its configuration turns out to be $\sigma_g^2(4s) \sigma_u^{*2}(4s) 3d^{13}$, and the $4s$ electron detachment would produce two possible states, with the same orbital configuration $\sigma_g^2(4s) \sigma_u^{*1}(4s) 3d^{13}$ but with the $\sigma_u^{*1}(4s)$ of high (${}^9\Sigma_g^-$) or low (${}^7\Sigma_g^-$) spin coupled to the remaining $3d^{13}$ electrons. These two states would correspond to the first and second peak of the spectrum, respectively, and display the same structural

properties, the only difference being the spin coupling. However, this interpretation disagrees with electron spin resonance experiments,[3] which fail to observe the Fe_2 and therefore supports the idea of an orbitally degenerate ground state, like the ${}^7\Delta_u$ configuration, unless the iron dimer features a large zero-field split (larger than 8 cm^{-1}), thus producing an energy split not detectable by the experimental setup. However, such a large magnetic split is unusual for that kind of molecules.

From the theoretical side, some numerical studies based mainly on density functional theory (DFT) methods with various functionals[4, 5, 6, 7] and multi reference configuration interaction (MRCI) calculations[8] yielded the ${}^7\Delta_u$ as the ground state of Fe_2 , while more recent MRCI calculations[9] and DFT studies with coupled cluster[10] and $+U$ [11] corrections supported the idea that its ground state is ${}^9\Sigma_g^-$. Those methods gave a ${}^8\Delta_g$ (${}^8\Sigma_u^-$) ground state for the anion whenever a ${}^7\Delta_u$ (${}^9\Sigma_g^-$) ground state was found for the neutral dimer.

In this Letter, we tackle the study of the iron dimer by means of quantum Monte Carlo (QMC) simulations based on the resonating valence bond (RVB) wave function,[12, 13] which is a correlated single-determinant ansatz successfully used in previous calculations.[14, 15, 16, 17] Here, we use an extension of the RVB picture that is based on a MO expansion of the singlet state in the determinant. By setting the number of MO's to a value such that a Jastrow correlated single determinant (SD) wave function is recovered for each fragment in the atomization limit, we obtain a description of the bond which is remarkably accurate. This ansatz has been tested on a set of first-row atom dimers, such as F_2 , N_2 , Be_2 , and C_2 , where our calculations yielded results for the binding energy and the equilibrium distance very close to the experimental values,[18] much better than those obtained in previous calculations based on standard Jastrow-SD (JSD) wave functions.[19]

Email address: michele.casula@gmail.com (Michele Casula)

2. Method

We consider a RVB wave function for N electrons, where for simplicity we take $N_\uparrow \geq N_\downarrow$, and N_\uparrow (N_\downarrow) is the number of spin up (down) electrons. The wavefunction is given by the product of a determinantal part and a Jastrow correlation factor. The determinantal part is the antisymmetrized product of singlet pairs. Each pair is described by a symmetric $\phi(\vec{r}, \vec{r}') = \phi(\vec{r}', \vec{r})$ orbital function. In order to define a pure spin state with total spin $S = |N_\uparrow - N_\downarrow|/2$ and maximum spin projection $S_z^{tot} = S$, we take N_\downarrow singlet pairs and $2S$ unpaired orbitals $\phi_j(\vec{r})$ for spin up electrons, and apply the antisymmetrization operator \mathcal{A} to obtain a consistent fermionic wave function:

$$\Phi_N(\vec{R}) = \mathcal{A} \prod_{i=1}^{N_\downarrow} \phi(\vec{r}_i^\uparrow, \vec{r}_i^\downarrow) \prod_{j=N_\downarrow+1}^{N_\uparrow} \phi_j(\vec{r}_j^\uparrow), \quad (1)$$

where Φ_N is the N -electron wave function and \vec{R} indicates the corresponding $3N$ -dimensional vector of coordinates, $\vec{R} = \{\vec{r}_1^\uparrow, \dots, \vec{r}_{N_\downarrow}^\uparrow, \vec{r}_1^\downarrow, \dots, \vec{r}_{N_\downarrow}^\downarrow\}$. The wave function in Eq. (1) is also called antisymmetrized geminal product (AGP) and can be computed by means of a single determinant (see Ref. [14] and references therein).

As said, the total spin of $\Phi_N(\vec{R})$ is definite. We also impose all possible symmetries to be satisfied, including angular momentum and spatial reflections.

The Jastrow correlation factor is the other important ingredient of the wavefunction. Its generally adopted form reads:

$$J(x) = \exp \left(\sum_{i < j} f(\vec{r}_i, \vec{r}_j) \right), \quad (2)$$

where $f(\vec{r}, \vec{r}')$ is a function of two electron coordinates.[15] The Jastrow term accounts for the electron-electron repulsion and suppresses configurations with overlapping valence bonds, which would lead to a too large electron density around an atom, with an increase in the total energy.

As any function of two coordinates, the pairing function ϕ as well as the correlation function f in the Jastrow term can be expanded in terms of single particle orbitals. In particular, the pairing function reads:

$$\phi(\vec{r}, \vec{r}') = \sum_{j=1}^{n-2S} \lambda_j \phi_j(\vec{r}) \phi_j(\vec{r}'), \quad (3)$$

where n is large enough, and $\{\phi_j\}$ is an orthogonal single particle basis set¹, which reaches its complete basis set limit for $n \rightarrow \infty$. Notice also that in these notations we assume that the $2S$ unpaired orbitals ϕ_j correspond to the indexes: $n - 2S + 1 \leq j \leq n$.

The single particle orbitals ϕ_j can be conveniently chosen as the MO's obtained with a conventional restricted Hartree-Fock (RHF) calculation. Indeed the MO basis allows us to write

¹The orbitals ϕ_i can be MO's expanded in terms of atomic orbitals $\varphi_{a,j}$ where a indicates the atomic center and j the type: $\phi_i(\vec{r}) = \sum_{a,j} \chi_{a,j}^i \varphi_{a,j}(\vec{r})$. The coefficients $\chi_{a,j}^i$, as well as the weights λ_j , can be used as variational parameters defining the geminal in Eq. (3)

Eq. (3) in a diagonal form equivalent to a more involved matrix form when the MO's are developed in an atomic basis set.[15] By truncating the expansion in Eq. (3) to a number of MO's n equal to the number of electron pairs and unpaired orbitals, namely $n = N_\uparrow$, one recovers the usual RHF theory, because the antisymmetrization operator \mathcal{A} clearly singles out only one Slater determinant. Moreover, the MO weights λ_j affect only an overall prefactor of this Slater determinant, so that their actual values are irrelevant in this case. However, the pairing function is generally not limited to have only N_\downarrow non vanishing eigenvalues λ_j . Therefore, the RVB wave function represents a clear extension of the RHF theory, not only for the presence of the Jastrow factor, which considerably improves the dynamical correlations, but mainly because its determinantal part goes beyond RHF when $n > N_\uparrow$, by including also non-dynamical correlations. Quite generally, a gain in energy and a more accurate calculation are expected whenever $n > N_\uparrow$.

In this Letter, we use in all calculations a number n^* of MO's that is enough to have a fully symmetric state that connects the compound at rest to the atoms at large distance, where a fragmented JSD wave function is recovered. A larger value of n certainly leads to a lower value of the total energy, but may improve much more the atomic energies, rather than the bonding.

Clearly, whenever $n = n^*$ the atomization energy has to be referenced to the JSD calculation, even when better energies are provided by the RVB for the atoms.[14] It is important to remark here that, upon stretching the molecule to the atomization limit, some symmetries of the atomic wave function are not recovered. For instance, for a diatomic molecule such as iron, the total angular momentum is conserved only for the rotations around the molecular axis, so that the total angular momentum of the atomic fragments could not be definite within this ansatz. Therefore, by assuming that this error does not affect the molecular bond, a correction to the atomic reference is necessary, given by the energy difference between the hybrid SD state reached upon stretching the RVB wave function and the fully symmetric JSD atomic state computed with the same primitive basis as the one used for the molecule.

Our RVB wave function is the input for QMC simulations. We start from its optimization, and then perform variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) simulations,[20] the latter within its recent lattice regularized implementation (LRDMC).[21] The optimization method used here is based on the calculations of the Hamiltonian matrix elements in the space spanned by the wave function[22, 23], recently developed to perform a constrained energy minimization with fixed n .[18]

3. Results

We compute the properties of the $^7\Delta_u$, $^7\Sigma_g^-$, $^9\Sigma_g^-$ states for the neutral dimer, with the method described in Sec. 2, namely with the idea that only a well controlled dissociation limit can lead to reliable predictions for the energetics in the bonding region. We also compute the $^8\Sigma_u^-$ and $^8\Delta_g$ states of the anion to make a direct comparison with the PES.

Table 1: Dissociation limits of various Fe_2 states for the RVB wave function. 5D (occupation $4s^23d^6$), and 5F (occupation $4s^13d^7$) refer to neutral atom states, while 4F (occupation $4s^23d^7$) is the ground state of the anion. The states denoted with $^{(2S+1)}[L_z]$ are non-definite angular momentum states for the presence of other components. They are eigenstate of L_z but not of L^2 . In particular $^4[0]$ and $^5[0]$ indicate the single occupation of the d orbitals with $l_z = \pm 2$ and $l_z = 0$, $^5[1]$ indicates the single occupation of the orbitals with $l_z = \pm 2$ and $l_z = -1$, while the remaining d orbitals are doubly occupied.

Fe_2 state	from our wf	exact
$^7\Sigma_g^- \rightarrow$	$^5D + ^5[1]$	$^5D + ^5F$
$^9\Sigma_g^- \rightarrow$	$^5D + ^5[0]$	$^5D + ^5F$
$^7\Delta_u \rightarrow$	$^5D + ^5[0]$	$^5D + ^5D$
$^8\Delta_g \rightarrow$	$^5D + ^4[0]$	$^5D + ^4F$
$^8\Sigma_u^- \rightarrow$	$^5D + ^4[0]$	$^5D + ^4F$

For all our calculations, we employ a neon-core pseudopotential, in order to avoid the chemically inert core electrons of the iron atom, and speed up the QMC simulations. We choose the Dolg’s pseudopotential,[24] which has previously proven to be reliable at least for atomic QMC calculations.[25] We use a $[8s5p6d/2s1p1d]$ contracted Gaussian basis set, which leads to a space spanned by 4 σ , 4 σ^* , 4 π , 4 π^* , 2 δ , and 2 δ^* MO’s, where we need to accommodate 32 electrons for the neutral dimer. Our primitive basis set is quite compact. However, we double checked the convergence in the energy differences for atomic calculations by extending the basis set up to $8s5p6d3f$. A much smaller basis was used for the Jastrow factor, because this allows for a more efficient energy optimization. On the other hand, the essentially exact contribution of Jastrow-type dynamical correlations, which do not change the phases of the wave function, can be very accurately obtained with DMC or LRDMC. The (LR)DMC approach can be seen as a stochastic optimization of a much more general Jastrow factor which keeps fixed the nodes of the RVB wave function.

For the $^9\Sigma_g^-$, $^8\Sigma_u^-$, and $^8\Delta_g$ states $n^* = N_\uparrow$ is such that the AGP is an HF Slater determinant, while for the $^7\Delta_u$ and the $^7\Sigma_g^-$ states $n^* = N_\uparrow + 1$, and the role of non-dynamical correlations becomes crucial in our optimization of the AGP. In fact the RVB provides in these latter cases a remarkable energy gain of more than 1 eV as compared with a more simple but much less accurate JSD calculation, at least as far as the agreement with experiments is concerned.

All the lowest possible configurations corresponding to states obtained after the dissociation of our wave function are reported in Table 1. It is apparent that non-dynamical correlations are very important in the compound whenever its total spin S is less than the total maximum spin of the fragments. As anticipated, a controlled atomic limit can be obtained also in this case, with the caveat that the total angular momentum L_z around the molecular axis is conserved in the atomization process. This implies that, within our RVB wave function, the total angular momentum L of the fragments may not be definite in the atomization limit, and the corresponding JSD atomic reference energies depend explicitly on the angular momentum projection quantum number L_z . In this way, we need to perform atomic

Table 2: The 5F , and 5D energies for the neutral atom, and the 4F energy for the anion are reported in Hartree. The non-definite angular momentum JSD states are denoted with the conventions reported in Table 1. They will be useful for the energy correction based on the dissociation limit. The variational wave function used here is a JSD like. From the total energies of the spin-definite states we calculate the $^5D \rightarrow ^5F$ excitations and the electron affinity, expressed in eV and compared with the experiment.

	LRDMC	exp.
5D	-123.7819(11)	
5F	-123.7520(11)	
$^5[0]$	-123.73986(72)	
$^5[1]$	-123.71856(75)	
4F	-123.77731(94)	
$^4[0]$	-123.76544(81)	
$^5D \rightarrow ^5F$ (eV)	0.81(4)	0.87 ^a
$^4F \rightarrow ^5D$ (eV)	-0.12(4)	0.15 ^a

^a From Ref. [27]

calculations for various L_z and choose the appropriate ones for the reference to the total energy of the dimer. The results of our atomic calculations are reported in Table 2. The $^5D \rightarrow ^5F$ transition is found to be very close to the experimental value, while the electron affinity is off by 0.3 eV. This is largely due to a lack of correlation energy in the LRDMC calculations for the anion, since MRCI calculations done with MOLPRO[26] are in agreement with the experimental value.

After performing LRDMC simulations for the iron dimer at different interatomic distances (going from 3.5 to 8) and symmetry states, we found the results reported in Table 3. The vibrational frequencies of $^9\Sigma_g^-$ and $^8\Sigma_g^-$ are in good agreement with the Leopold’s experimental data. Indeed, our best QMC estimate for the vibrational frequency of the Fe_2 ground state is $\omega_e = 301(15)\text{cm}^{-1}$, which matches perfectly the value $300(15)\text{cm}^{-1}$ coming from PES,[1] and the value 299.6cm^{-1} provided by Raman spectroscopy.[28] Also for the anion dimer the LRDMC vibrational frequency ($\omega_e = 210(20)\text{cm}^{-1}$) agrees with the experimental value of $250(25)\text{cm}^{-1}$ yielded by PES.[1] Notice that our calculations correctly reproduce the softening of the vibrational mode going from $^9\Sigma_g^-$ to $^8\Sigma_g^-$. Therefore, from these results we can confirm the symmetry of the peaks seen in the PES. Indeed, the $^7\Delta_u$ state has a much higher vibrational frequency, incompatible with the experiment. It is interesting to highlight that the vibrational frequency for $^7\Delta_u$ computed with QMC simulations agrees with those calculated by DFT methods for the same states.[6, 7] To check whether the $^9\Sigma_g^-$ is the true ground state, let us apply the correction to the energy levels based on the atomization limits. To do so, we add to the total energy of the dimer the atomic energy differences between the right (the exact fully symmetric JSD limit) and the middle column (the asymptotic JSD limit that is possible to reach within our wave function) of Table 1.

The level ordering that we find is reported in Table 4. It turns out that after the correction the $^7\Delta_u$ is the actual ground state, while the energy split between the $^9\Sigma_g^-$ and the $^7\Sigma_g^-$ states is 0.64(7) eV, in quite good agreement with the experimental

Table 3: The LRDMC results are reported for some states of the neutral iron dimer, and for the anion states $^8\Sigma_u^-$ and $^8\Delta_g$. We calculated total energies at the minimum of the interatomic potential, equilibrium distances R_e , and vibrational frequencies ω_e . Some available experimental values are also reported.

	Energy (Hartree)	R_e (a.u.)	ω_e (cm^{-1})	exp ω_e (cm^{-1})
$^7\Sigma_g^-$	-247.5036(20)	4.081(18)	327(15)	300(15) ^b
$^9\Sigma_g^-$	-247.5486(20)	4.093(19)	301(15)	299.6 ^a
$^7\Delta_u$	-247.5351(30)	3.894(18)	373(32)	-
$^8\Delta_g$	-247.5585(30)	3.908(14)	354(24)	-
$^8\Sigma_u^-$	-247.5706(42)	4.276(28)	210(20)	250(20) ^b

^a From Ref. [28]

^b From Ref. [1]

findings (0.534(4) eV).[1] The correction does not change the ordering for the anion, and so its ground state remains the $^8\Sigma_u^-$. This is a quite interesting effect of the correlation, which acts on the d orbitals in a way which depends on the global symmetry and total charge of the system. This is apparent already at the atomic level, where the occupation of the d orbitals changes by going from the 4F anion to the neutral 5D ground states. The energy difference between the anion $^8\Sigma_u^-$ state and the neutral $^9\Sigma_g^-$ is 0.59(12) eV, which should be further shifted by 0.3 eV due to the electron affinity correction in the atomic calculations, because for this quantity the JSD is rather poor, as we have previously shown in Table 2. This will lead to a difference of ≈ 0.9 eV between the two states, again in agreement with the experimental value of 0.902(8) eV.[1] This suggests that our approach can be further improved by replacing the reference JSD atomization energies with exact atomic energies, readily available in quantum chemistry databases. This approach is clearly useful and practical when one needs to consider total energy differences between electronic states with different particle number, like the electron affinity and ionization energies. We would like to stress that, although the correction based on the asymptotic limits is “approximate”, the accuracy level reachable in this way (≈ 0.1 , maximum 0.2 eV) is below the final energy differences.[18] Therefore, the ordering we propose here can be taken with a good confidence.

Table 4: The results for the energy minimum are reported for the same states as in Table 3, but with the correction described in the text which takes into account the atomic limit of the wave functions. In the last two columns, we report the energy differences with respect to the state $^9\Sigma_g^-$ after the correction, and the experimental values taken from the Leopold’s experiment.

	Energy (Hartree)	Corrected (Hartree)	Difference (eV)	Exp (eV)
$^7\Sigma_g^-$	-247.5036(20)	-247.5370(24)	+0.64(7)	+0.534(4) ^a
$^9\Sigma_g^-$	-247.5486(20)	-247.5608(24)	0.0	
$^7\Delta_u$	-247.5351(30)	-247.5771(33)	-0.44(9)	-
$^8\Delta_g$	-247.5585(30)	-247.5703(33)	-0.26(9)	-
$^8\Sigma_u^-$	-247.5706(42)	-247.5824(44)	-0.59(12)	-0.902(8) ^a

^a From Ref. [1]

Notice that the determination of the $^7\Delta_u$ as the ground state is also supported by the equilibrium bond lengths provided by our calculations. Indeed, the experimental bond length is 3.82(4),[29] which is very close to our findings for the $^7\Delta_u$ (see Table 3). On the other hand, the bond length of the anion has been measured only indirectly, since the unique available data are taken from the PES, which revealed a *variation* of the equilibrium distance during the excitation from the anion to the neutral iron dimer. A harmonic Franck-Condon analysis of the vibronic band intensity profile yielded a bond elongation of 0.15(4) a.u. on electron attachment.[1] Now, the difference between the $^9\Sigma_g^-$ and $^8\Sigma_u^-$ bond length of our LRDMC calculation amounts to 0.18 a.u., which is in perfect agreement with the elongation of the anion dimer measured in the PES. Therefore, we conclude that the states seen in the Leopold’s photoelectron spectrum are the anion $^8\Sigma_u^-$, and the neutral $^9\Sigma_g^-$ and $^7\Sigma_g^-$. The ground state of the neutral dimer is however the $^7\Delta_u$ state, not seen in the photoelectron experiment since the transition from a $^8\Sigma_u^-$ (the anion symmetry of the prepared initial state) to a $^7\Delta_u$ symmetry is a second-order process, and so of negligible rate with respect to the $^9\Sigma_g^-$ and $^7\Sigma_g^-$ states, connected with the $^8\Sigma_u^-$ by a direct photodetachment of the electron living in the $4\sigma^*(4s)$ orbital.[2]

4. Conclusions

We have shown that by using a cheap and nevertheless very accurate realization of the RVB wave function based on the MO expansion of the AGP part, it is possible to tackle highly debated and challenging transition metal compounds. The solution of the iron dimer puzzle appears at end, and we strongly believe that many other problems - where the electron correlation plays a strong role - could be finally understood within this framework.

Acknowledgments

This work was partially supported by COFIN2007, and CNR. One of us (M.C.) acknowledges support in the form of the NSF grant DMR-0404853 during his stay at the University of Illinois at Urbana-Champaign, and thanks the Centre de Physique Théorique of the Ecole Polytechnique, where this work was partially accomplished. We acknowledge useful discussions with N. Marzari, H. Kulik, L. Mitas, and L. Guidoni.

References

- [1] D. G. Leopold, W. C. Lineberger, The Journal of Chemical Physics 85 (1) (1986) 51–55.
- [2] D. G. Leopold, J. Almlöf, W. C. Lineberger, P. R. Taylor, The Journal of Chemical Physics 88 (6) (1988) 3780–3783.
- [3] C. A. Baumann, R. J. Van Zee, W. Weltner Jr., The Journal of Physical Chemistry 88 (1984) 1815–1820.
- [4] M. Castro, D. R. Salahub, Physical Review B 47 (16) (1993) 10955–10958.
- [5] M. Castro, D. R. Salahub, Physical Review B 49 (17) (1994) 11842–11852.
- [6] S. Chrétien, D. R. Salahub, Physical Review B 66 (15) (2002) 155425–1–155425–12.

- [7] G. L. Gutsev, C. W. Bauschlicher Jr., *The Journal of Physical Chemistry A* 107 (2003) 7013–7023.
- [8] H. Tatewaki, M. Tomonari, T. Nakamura, *The Journal of Chemical Physics* 88 (10) (1988) 6419–6430.
- [9] O. Hübner, J. Sauer, *Chemical Physics Letters* 358 (2002) 442–448.
- [10] A. Irigoras, M. del Carmen Michelini, E. Sicili, N. Russo, J. M. Mercero, J. M. Ugalde, *Chemical Physics Letters* 376 (2003) 310–317.
- [11] H. J. Kulik, M. Cococcioni, D. A. Scherlis, N. Marzari, *Physical Review Letters* 97 (10) 103001–1–103001–4.
- [12] L. Pauling, *The nature of the chemical bond*, 3rd Edition, Cornell University Press, Ithaca, New York, 1979.
- [13] P. W. Anderson, *Science* 235 (1987) 1196–1198.
- [14] M. Casula, S. Sorella, *The Journal of Chemical Physics* 119 (13) (2003) 6500–6511.
- [15] M. Casula, C. Attaccalite, S. Sorella, *The Journal of Chemical Physics* 121 (15) (2004) 7110–7126.
- [16] M. Bajdich, L. Mitas, G. Drobný, L. K. Wagner, K. E. Schmidt, *Physical Review Letters* 96 (13) (2006) 130201–1–130201–4.
- [17] M. Bajdich, L. Mitas, L. K. Wagner, K. E. Schmidt, *Physical Review B (Condensed Matter and Materials Physics)* 77 (11) (2008) 115112–1–115112–13.
- [18] M. Marchi, S. Azadi, M. Casula, S. Sorella, in preparation.
- [19] J. C. Grossman, *The Journal of Chemical Physics* 117 (4) (2002) 1434–1440.
- [20] W. M. C. Foulkes, L. Mitas, R. J. Needs, G. Rajagopal, *Review of Modern Physics* 73 (1) (2001) 33–83.
- [21] M. Casula, C. Filippi, S. Sorella, *Physical Review Letters* 95 (10) (2005) 100201–1–100201–4.
- [22] C. J. Umrigar, J. Toulouse, C. Filippi, S. Sorella, R. G. Hennig, *Physical Review Letters* 98 (10) 110201–1–110201–4.
- [23] S. Sorella, M. Casula, D. Rocca, *The Journal of Chemical Physics* 127 (1) (2007) 014105–1–014105–12.
- [24] M. Dolg, U. Wedig, H. Stoll, H. Preuss, *The Journal of Chemical Physics* 86 (2) (1987) 866–872.
- [25] L. Mitáš, *Physical Review A* 49 (6) (1994) 4411–4414.
- [26] H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, et al., *Molpro*, version 2008.1, a package of ab initio programs, see <http://www.molpro.net> (2008).
- [27] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circ. No. 467, U.S. GPO, Washington, D.C., 1949.
- [28] M. Moskovits, D. P. DiLella, *The Journal of Chemical Physics* 73 (10) (1980) 4917–4924.
- [29] H. Purdum, P. A. Montano, G. K. Shenoy, T. Morrison, *Physical Review B* 25 (7) (1982) 4412–4417.